

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 883 022 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**09.08.2000 Bulletin 2000/32**

(51) Int Cl.7: **G03C 1/74, G03C 1/498,  
B41M 5/32**

(21) Application number: **98109374.3**

(22) Date of filing: **22.05.1998**

(54) **Coating method for thermographic imaging element, coating solution for thermographic image forming layer, thermographic imaging element, and photothermographic imaging element**

Beschichtungsverfahren für ein thermographisches Bildaufzeichnungselement, Beschichtungslösung für eine thermographische Bildaufzeichnungsschicht, thermographisches Bildaufzeichnungselement und photothermographisches Bildaufzeichnungselement

Procédé de revêtement pour un élément thermographique formateur d'image, solution de revêtement pour une couche thermographique formatrice d'image, élément thermographique formateur d'image et élément photothermographique formateur d'image

(84) Designated Contracting States:  
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE**

(30) Priority: **06.06.1997 JP 16499397  
15.10.1997 JP 29788797**

(43) Date of publication of application:  
**09.12.1998 Bulletin 1998/50**

(73) Proprietor: **FUJI PHOTO FILM CO., LTD.  
Kanagawa-ken (JP)**

(72) Inventors:  
• **Tsuzuki, Hirohiko  
Minami-Ashigara-shi, Kanagawa (JP)**

• **Higashiyama, Masaaki  
Minami-Ashigara-shi, Kanagawa (JP)**

(74) Representative:  
**Hansen, Bernd, Dr. Dipl.-Chem. et al  
Hoffmann Eitle,  
Patent- und Rechtsanwälte,  
Arabellastrasse 4  
81925 München (DE)**

(56) References cited:  
**EP-A- 0 628 862 EP-A- 0 773 472  
US-A- 4 113 903**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 0 883 022 B1**

**Description**

**[0001]** This invention relates to a coating method for the preparation of a thermographic imaging element, a coating solution for a thermographic image forming layer, a thermographic imaging element, and a photothermographic imaging element.

**BACKGROUND OF THE INVENTION**

**[0002]** From the contemporary standpoints of environmental protection and space saving, it is strongly desired in the medical imaging field to reduce the quantity of spent solution. Needed in this regard is a technology relating to thermographic photosensitive materials for use in medical diagnosis and general photography which can be effectively exposed by means of laser image setters and laser imagers and produce clear black images having a high resolution and sharpness. These thermographic photosensitive materials offer to the customer a simple thermographic system which eliminates a need for solution type chemical agents and is not detrimental to the environment.

**[0003]** While a similar requirement is sometimes raised in the general imaging material field, medical images require high definition, that is, high image quality characterized by excellent sharpness and graininess. From the standpoint of ease of diagnosis, blue black tone images are favorable. At present, various hard copy systems using pigments and dyes such as ink jet printers and electrophotographic printers are widely marketed as the image forming system, but none of them are satisfactory as the output system for medical images.

**[0004]** Thermal image forming systems utilizing organic silver salts are disclosed in the literature, for example, USP 2,910,377 and JP-B 4924/1968. These thermal image forming systems utilizing organic silver salts can produce images of quality and tone regarded satisfactory as medical images. Since coating solutions having high liquidity are generally used, however, there is the problem that the wind during drying tends to cause surface failure or wind-swept unevenness. If highly viscous coating solutions are used in order to prohibit the wind-swept unevenness, the ease of coating is lost and streaky failure occurs. A common practice for finding a compromise between these failures is to reduce the wind velocity of drying air, which can compromise the drying ability and hence, rapid coating.

**[0005]** EP-A-7 734 472 describes a method of increasing the maximum coating speed and a coating formulation comprising a dispersion of colloidal particles is a hydrophilic colloid.

**[0006]** US-A-4 113 903 describes a process of applying a multilayer liquid coating to a moving web comprising applying a shear thinning carrier layer of pseudoplastic liquid.

**[0007]** On the other hand, conventional photographic photo-sensitive materials solve a similar problem by using gelatin as the binder and after coating, quenching the coating to cause the gelatin to gel. If gelatin is used in the image forming layer of thermographic imaging elements, no material diffusion occurs in a heated state during similar processing, and image formation is substantially retarded.

**SUMMARY OF THE INVENTION**

**[0008]** An object of the invention is to provide a novel and improved coating method capable of forming a coated thermographic imaging element having improved surface quality at a high speed of coating and at no sacrifice of image forming ability. Another object of the invention is to provide a coating solution for a thermographic image forming layer. A further object of the invention is to provide a thermographic imaging element and a photothermographic imaging element.

**[0009]** According to a first aspect of the invention, there is provided a coating method for the preparation of a thermographic or photothermographic imaging element, comprising the step of applying a liquid containing an organic silver salt and a binder. The liquid is pre-adjusted to a viscosity at 25°C of 500 mPa·s to 500,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup> and 0.1 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.

**[0010]** The organic silver salt is typically a silver salt of an organic carboxylic acid. Preferably, the liquid further contains a reducing agent for silver ion and optionally, a photosensitive silver halide.

**[0011]** According to a second aspect of the invention, there is provided a coating solution for forming a thermographic image forming layer, containing an organic silver salt, a reducing agent for silver ion, and a binder and having a viscosity at 25°C of 500 mPa·s to 500,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup> and 0.1 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.

**[0012]** According to a third aspect of the invention, there is provided a thermographic (heat sensitive) imaging element which has been prepared by applying a coating solution containing an organic silver salt, a reducing agent for silver ion, and a binder and having a viscosity at 25°C of 500 mPa·s to 500,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup> and 0.1 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.

**[0013]** According to a fourth aspect of the invention, there is provided a photothermographic (photosensitive heat-developable) imaging element which has been prepared by applying a coating solution containing an organic silver salt, a reducing agent for silver ion, a photosensitive silver halide, and a binder and having a viscosity at 25°C of 500

mPa·s to 500,000 mPa·s at a shear rate of  $0.1 \text{ s}^{-1}$  and 0.1 mPa·s to 100 mPa·s at a shear rate of  $1,000 \text{ s}^{-1}$ .

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The only figure, FIG. 1 is a partially cross-sectional, side elevation of a coater used in Example 1.

#### DETAILED DESCRIPTION OF THE INVENTION

[0015] The coating solution of interest contains an organic silver salt.

##### Organic silver salt

[0016] The organic silver salt which can be used herein is relatively stable to light, but forms a silver image when heated at  $80^{\circ}\text{C}$  or higher in the presence of an exposed photocatalyst (as typified by a latent image of photo-sensitive silver halide) and a reducing agent. The organic silver salt may be of any desired organic compound containing a source capable of reducing silver ion. Preferred are silver salts of organic acids, more preferably silver salts of organic carboxylic acids, typically silver salts of long chain aliphatic carboxylic acids having 10 to 30 carbon atoms, especially 15 to 28 carbon atoms. Also preferred are complexes of organic or inorganic silver salts with ligands having a stability constant in the range of 4.0 to 10.0. A silver-providing substance is preferably used in an amount of about 5 to 70% by weight of an image forming layer. Preferred organic silver salts include silver salts of organic compounds having a carboxyl group. Examples include silver salts of aliphatic carboxylic acids and silver salts of aromatic carboxylic acids though not limited thereto. Preferred examples of the silver salt of aliphatic carboxylic acid include silver behenate, silver arachidate, silver stearate, silver oleate, silver laurate, silver caproate, silver myristate, silver palmitate, silver maleate, silver fumarate, silver tartrate, silver linolate, silver butyrate, silver camphorate and mixtures thereof.

[0017] Silver salts of compounds having a mercapto or thion group and derivatives thereof are also useful. Preferred examples of these compounds include a silver salt of 3-mercapto-4-phenyl-1,2,4-triazole, a silver salt of 2-mercapto-benzimidazole, a silver salt of 2-mercapto-5-aminothiadiazole, a silver salt of 2-(ethylglycolamido)-benzothiazole, silver salts of thioglycolic acids such as silver salts of S-alkylthioglycolic acids wherein the alkyl group has 12 to 22 carbon atoms, silver salts of dithiocarboxylic acids such as a silver salt of dithioacetic acid, silver salts of thioamides, a silver salt of 5-carboxyl-1-methyl-2-phenyl-4-thiopyridine, silver salts of mercaptotriazines, a silver salt of 2-mercaptobenzoxazole as well as silver salts of 1,2,4-mercaptotriazole derivatives such as a silver salt of 3-amino-5-benzylthio-1,2,4-thiazole as described in USP 4,123,274 and silver salts of thion compounds such as a silver salt of 3-(3-carboxyethyl)-4-methyl-4-thiazoline-2-thione as described in USP 3,301,678. Compounds containing an imino group may also be used. Preferred examples of these compounds include silver salts of benzotriazole and derivatives thereof, for example, silver salts of benzotriazoles such as silver methylbenzotriazole, silver salts of halogenated benzotriazoles such as silver 5-chlorobenzotriazole as well as silver salts of 1,2,4-triazole and 1-H-tetrazole and silver salts of imidazole and imidazole derivatives as described in USP 4,220,709. Also useful are various silver acetylide compounds as described, for example, in USP 4,761,361 and 4,775,613.

[0018] The organic silver salt which can be used herein may take any desired shape although needle crystals having a minor axis and a major axis are preferred. In the practice of the invention, grains should preferably have a minor axis of  $0.01 \mu\text{m}$  to  $0.20 \mu\text{m}$ , more preferably  $0.01 \mu\text{m}$  to  $0.15 \mu\text{m}$  and a major axis of  $0.10 \mu\text{m}$  to  $5.0 \mu\text{m}$ , more preferably  $0.10 \mu\text{m}$  to  $4.0 \mu\text{m}$ . The grain size distribution is desirably monodisperse. The monodisperse distribution means that a standard deviation of the length of minor and major axes divided by the length, respectively, expressed in percent, is preferably up to 100%, more preferably up to 80%, most preferably up to 50%. It can be determined from the measurement of the shape of organic silver salt grains using an image obtained through a transmission electron microscope. Another method for determining a monodisperse distribution is to determine a standard deviation of a volume weighed mean diameter. The standard deviation divided by the volume weighed mean diameter, expressed in percent, which is a coefficient of variation, is preferably up to 100%, more preferably up to 80%, most preferably up to 50%. It may be determined by irradiating laser light, for example, to organic silver salt grains dispersed in liquid and determining the autocorrelation function of the fluctuation of scattering light relative to a time change, and obtaining the grain size (volume weighed mean diameter) therefrom.

[0019] The organic silver salt used herein is preferably desalted. The desalting method is not critical. Any well-known method may be used although well-known filtration methods such as centrifugation, suction filtration, ultrafiltration, and flocculation/water washing are preferred.

[0020] In the practice of the invention, the organic silver salt is prepared into a solid microparticulate dispersion using a dispersant, in order to provide fine particles of small size and free of flocculation. A solid microparticulate dispersion of the organic silver salt may be prepared by mechanically dispersing the salt in the presence of dispersing aids by well-known comminuting means such as ball mills, vibrating ball mills, planetary ball mills, sand mills, colloidal mills,

jet mills, roller mills, microliquidizers, nanomizers, and Gaulin homogenizers. Preferred are micro-liquidizers, nanomizers, and Gaulin homogenizers.

**[0021]** The dispersant used in the preparation of a solid microparticulate dispersion of the organic silver salt may be selected from synthetic anionic polymers such as polyacrylic acid, copolymers of acrylic acid, copolymers of maleic acid, copolymers of maleic acid monoester, and copolymers of acryloylmethylpropanesulfonic acid; semi-synthetic anionic polymers such as carboxymethyl starch and carboxymethyl cellulose; anionic polymers such as alginic acid and pectic acid; anionic surfactants as described in JP-A 92716/1977 and WO 88/04794; the compounds described in Japanese Patent Application No. 350753/1995; well-known anionic, nonionic and cationic surfactants; and well-known polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, carboxymethyl cellulose, hydroxypropyl cellulose, and hydroxypropyl methylcellulose, as well as naturally occurring high molecular weight compounds such as gelatin.

**[0022]** In general, the dispersant is mixed with the organic silver salt in powder or wet cake form prior to dispersion. The resulting slurry is fed into a dispersing machine. Alternatively, a mixture of the dispersant with the organic silver salt is subject to heat treatment or solvent treatment to form a dispersant-bearing powder or wet cake of the organic silver salt. It is acceptable to effect pH control with a suitable pH adjusting agent before, during or after dispersion.

**[0023]** Rather than mechanical dispersion, fine particles can be formed by roughly dispersing the organic silver salt in a solvent through pH control and thereafter, changing the pH in the presence of dispersing aids. An organic solvent can be used as the solvent for rough dispersion although the organic solvent is usually removed at the end of formation of fine particles.

**[0024]** The thus prepared dispersion may be stored while continuously stirring for the purpose of preventing fine particles from settling during storage. Alternatively, the dispersion is stored after adding hydrophilic colloid to establish a highly viscous state (for example, in a jelly-like state using gelatin). An antiseptic agent may be added to the dispersion in order to prevent the growth of bacteria during storage.

**[0025]** The organic silver salt is used in any desired amount, preferably 0.1 to 5 g per square meter of the imaging element, more preferably 1 to 3 g/m<sup>2</sup>.

**[0026]** The liquid containing the organic silver salt according to the invention, which is also designated a coating solution for forming a thermographic image forming layer, is a thixotropic fluid. Thixotropy is a structural property that a gel reduces its viscosity as the shear rate increases.

**[0027]** In measuring the viscosity of a liquid, any meter may be used. A fluid spectrometer RFS commercially available from Rheometrics Far East K.K. is preferred. Viscosity measurement is made at 25°C.

**[0028]** The organic silver salt-containing liquid or thermographic image forming layer coating solution according to the invention has a viscosity of 500 mPa·s to 500,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup>, preferably 500 to 300,000 mPa·s, more preferably 1,000 to 100,000 mPa·s, and most preferably 1,000 to 30,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup>. The liquid also has a viscosity of 0.1 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>, preferably 0.2 to 100 mPa·s, and more preferably 1 to 80 mPa·s at a shear rate of 1,000 s<sup>-1</sup>. It is noted that coating solutions for use in the preparation of conventional photographic photosensitive materials and photothermographic materials using benzotriazole silver salts have a viscosity of about 20 to 100 mPa·s at a shear rate of 0.1 s<sup>-1</sup> and about 5 to 50 mPa·s at a shear rate of 1,000 s<sup>-1</sup>, and coating solutions for use in the preparation of photothermographic materials using silver behenate have a viscosity of about 100 to 300 mPa·s both at a shear rate of 0.1 s<sup>-1</sup> and 1,000 s<sup>-1</sup>. These prior art solutions are not thixotropic.

**[0029]** A variety of systems are known to exert thixotropy. Reference should be made to, for example, Kobunshi Kankokai Ed., "Rheology," and Muroi and Morino, "Polymer Latex," (published by Kobunshi Kankokai). In order for a liquid to exert thixotropy, the liquid should contain a multiplicity of fine solid particles. Thixotropy can be enhanced by containing thickening linear polymers, using fine solid particles having anisotropy and a high aspect ratio, or using alkaline thickening agents or surfactants.

**[0030]** An appropriate means for providing thixotropy in the practice of the invention is to admit fine solid particles having a size of 0.001 µm to 10 µm, especially 0.01 µm to 5 µm into the organic silver salt-containing liquid or thermographic image forming layer coating solution in a concentration of 10 to 80% by weight, preferably 15 to 50% by weight, especially 20 to 50% by weight. It is preferred that fine solid particles of at least one type be tabular or acicular rather than spherical. More preferably such non-spherical fine solid particles are contained in a concentration of 0.1 to 50% by weight, especially 0.5 to 20% by weight of the coating solution. The fine solid particles may be of the organic silver salt, reducing agent, binder or antifoggant.

#### Reducing agent

**[0031]** The organic silver salt-containing liquid or thermographic image forming layer coating solution according to the invention contains a reducing agent for the organic silver salt. The reducing agent for the organic silver salt may be any of substances, preferably organic substances, that reduce silver ion into metallic silver. Conventional photographic developing agents such as Phenidone®, hydroquinone and catechol are useful although hindered phenols are

preferred reducing agents. The reducing agent should preferably be contained in an amount of 5 to 50 mol%, more preferably 10 to 40 mol% per mol of silver on the image forming layer-bearing side. The reducing agent may take the form of a precursor which is modified so as to exert its effective function only at the time of development.

[0032] For photothermographic materials using organic silver salts, a wide range of reducing agents are disclosed, for example, in JP-A 6074/1971, 1238/1972, 33621/1972, 46427/1974, 115540/1974, 14334/1975, 36110/1975, 147711/1975, 32632/1976, 1023721/1976, 32324/1976, 51933/1976, 84727/1977, 108654/1980, 146133/1981, 82828/1982, 82829/1982, 3793/1994, USP 3,667,958, 3,679,426, 3,751,252, 3,751,255, 3,761,270, 3,782,949, 3,839,048, 3,928,686, 5,464,738, German Patent No. 2321328, and EP 692732. Exemplary reducing agents include amidoximes such as phenylamidoxime, 2-thienylamidoxime, and p-phenoxyphenylamidoxime; azines such as 4-hydroxy-3,5-dimethoxybenzaldehydeazine; combinations of aliphatic carboxylic acid arylhydrazides with ascorbic acid such as a combination of 2,2-bis(hydroxymethyl)propionyl- $\beta$ -phenylhydrazine with ascorbic acid; combinations of polyhydroxybenzenes with hydroxylamine, reductone and/or hydrazine, such as combinations of hydroquinone with bis(ethoxyethyl)hydroxylamine, piperidinohexosereductone or formyl-4-methylphenylhydrazine; hydroxamic acids such as phenylhydroxamic acid, p-hydroxyphenylhydroxamic acid, and  $\beta$ -anilinehydroxamic acid; combinations of azines with sulfonamidophenols such as a combination of phenothiazine with 2,6-dichloro-4-benzenesulfonamidephenol;  $\alpha$ -cyanophenyl acetic acid derivatives such as ethyl- $\alpha$ -cyano-2-methylphenyl acetate and ethyl- $\alpha$ -cyanophenyl acetate; bis- $\beta$ -naphthols such as 2,2-dihydroxy-1,1-binaphthyl, 6,6-dibromo-2,2-dihydroxy-1,1-binaphthyl, and bis(2-hydroxy-3-t-butyl-5-methylphenyl)methane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 4,4-ethylidene-bis(2-t-butyl-6-methylphenol), 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, and 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane; ascorbic acid derivatives such as 1-ascorbyl palmitate and ascorbyl stearate; aldehydes and ketones such as benzil and diacetyl; 3-pyrazolidones and certain indane- and chromanols (tocopherols). Preferred reducing agents are bisphenols and chromanols.

[0033] The reducing agent may be added in any desired form such as solution, powder or solid particle dispersion. The solid particle dispersion of the reducing agent may be prepared by well-known comminuting means such as ball mills, vibrating ball mills, sand mills, colloidal mills, jet mills, and roller mills. Dispersing aids may be used for facilitating dispersion.

#### Polymer latex

[0034] By applying the organic silver salt-containing liquid or thermographic image forming layer coating solution according to the invention, there is formed an image forming layer which should preferably contain a polymer latex in an amount of at least 50% by weight based on the entire binder. Hereinafter, this image forming layer is often designated "inventive image forming layer," and the polymer latex used as the binder is often designated "inventive polymer latex." The "polymer latex" is a dispersion of a microparticulate water-insoluble hydrophobic polymer in a water-soluble dispersing medium. With respect to the dispersed state, a polymer emulsified in a dispersing medium, an emulsion polymerized polymer, a micelle dispersion, and a polymer having a hydrophilic structure in a part of its molecule so that the molecular chain itself is dispersed on a molecular basis are included. With respect to the polymer latex, reference is made to Okuda and Inagaki Ed., "Synthetic Resin Emulsion," Kobunshi Kankokai, 1978; Sugimura, Kataoka, Suzuki and Kasahara Ed., "Application of Synthetic Latex," Kobunshi Kankokai, 1993; and Muroi, "Chemistry of Synthetic Latex," Kobunshi Kankokai, 1970. Dispersed particles should preferably have a mean particle size of 1 to 50,000 nm, more preferably 5 to 1,000 nm. No particular limit is imposed on the particle size distribution of dispersed particles, and the dispersion may have either a wide particle size distribution or a monodisperse particle size distribution.

[0035] The polymer latex used herein may be either a latex of the conventional uniform structure or a latex of the so-called core/shell type. In the latter case, better results are sometimes obtained when the core and the shell have different glass transition temperatures.

[0036] The polymer latex should preferably have a minimum film-forming temperature (MFT) of -30°C to 90°C, more preferably 0°C to 70°C. A film-forming aid may be added in order to control the minimum film-forming temperature. The film-forming aid is also referred to as a plasticizer and includes organic compounds (typically organic solvents) for lowering the minimum film-forming temperature of a polymer latex. It is described in Muroi, "Chemistry of Synthetic Latex," Kobunshi Kankokai, 1970.

[0037] Polymers used in the polymer latex according to the invention include acrylic resins, vinyl acetate resins, polyester resins, polyurethane resins, rubbery resins, vinyl chloride resins, vinylidene chloride resins, polyolefin resins,

and copolymers thereof. The polymer may be linear or branched or crosslinked. The polymer may be either a homopolymer or a copolymer having two or more monomers polymerized together. The copolymer may be either a random copolymer or a block copolymer. The polymer preferably has a number average molecule weight  $M_n$  of 5,000 to 1,000,000, more preferably 10,000 to 100,000. Polymers with a too lower molecular weight would generally provide a low film strength after coating whereas polymers with a too higher molecular weight are difficult to form films.

[0038] The polymer of the polymer latex used herein should preferably have an equilibrium moisture content at 25°C and RH 60% of up to 2% by weight, more preferably up to 1% by weight. With respect to the definition and measurement of equilibrium moisture content, reference should be made to "Polymer Engineering Series No. 14, Polymer Material Test Methods," Edited by Japanese Polymer Society, Chijin Shokan Publishing K.K., for example.

[0039] Illustrative examples of the polymer latex which can be used as the binder in the image forming layer of the photothermographic material of the invention include latexes of methyl methacrylate/ethyl acrylate/methacrylic acid copolymers, latexes of methyl methacrylate/2-ethylhexyl acrylate/styrene/acrylic acid copolymers, latexes of styrene/butadiene/acrylic acid copolymers, latexes of styrene/butadiene/divinyl benzene/methacrylic acid copolymers, latexes of methyl methacrylate/vinyl chloride/acrylic acid copolymers, and latexes of vinylidene chloride/ethyl acrylate/acrylonitrile/methacrylic acid copolymers.

[0040] These polymers or polymer latexes are commercially available. Exemplary acrylic resins are Sebian A-4635, 46583 and 4601 (Daicell Chemical Industry K.K.) and Nipol LX811, 814, 820, 821 and 857 (Nippon Zeon K.K.). Exemplary polyester resins are FINETEX ES650, 611, 675, and 850 (Dai-Nihon Ink Chemical K.K.) and WD-size and WMS (Eastman Chemical Products, Inc.). Exemplary polyurethane resins are HYDRAN AP10, 20, 30 and 40 (Dai-Nihon Ink Chemical K.K.). Exemplary rubbery resins are LACSTAR 7310K, 3307B, 4700H and 7132C (Dai-Nihon Ink Chemical K.K.) and Nipol LX416, 410, 438C and 2507 (Nippon Zeon K.K.). Exemplary vinyl chloride resins are G351 and G576 (Nippon Zeon K.K.). Exemplary vinylidene chloride resins are L502 and L513 (Asahi Chemicals K.K.). Exemplary olefin resins are Chemipearl S120 and SA100 (Mitsui Petro-Chemical K.K.). These polymers may be used alone or in admixture of two or more.

[0041] In the organic silver salt-containing liquid or thermographic image forming layer coating solution according to the invention, the polymer latex described above is used in an amount of at least 50% by weight, especially at least 70% by weight, of the entire binder. In the organic silver salt-containing liquid or thermographic image forming layer coating solution, a hydrophilic polymer may be added in an amount of less than 50% by weight of the entire binder. Such hydrophilic polymers are gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, and hydroxypropyl methyl cellulose. The amount of the hydrophilic polymer added is preferably less than 30% by weight of the entire binder in the image forming layer.

[0042] The organic silver salt-containing liquid or thermographic image forming layer coating solution according to the invention is preferably aqueous. By the term "aqueous", it is meant that water accounts for at least 30% by weight of the solvent or dispersing medium of the coating solution. The component other than water of the coating solution may be a water-miscible organic solvent such as methyl alcohol, ethyl alcohol, isopropyl alcohol, methyl cellosolve, ethyl cellosolve, dimethylformamide, and ethyl acetate. Exemplary solvent compositions include a 90/10 or 70/30 mixture of water/methanol, a 90/10 mixture of water/ethanol, a 90/10 mixture of water/isopropanol, a 95/5 mixture of water/dimethylformamide, a 80/15/5 or 90/5/5 mixture of water/methanol/dimethylformamide, all expressed in a weight ratio.

[0043] In the image forming layer according to the invention, the total amount of binder is preferably 0.2 to 30 g/m<sup>2</sup>, more preferably 1 to 15 g/m<sup>2</sup> per layer. To the image forming layer, crosslinking agents for crosslinking, surfactants for ease of application, and other addenda may be added.

#### Silver halide

[0044] A method for forming the photosensitive silver halide is well known in the art. Any of the methods disclosed in Research Disclosure No. 17029 (June 1978) and USP 3,700,458, for example, may be used. Illustrative methods which can be used herein are a method of preparing an organic silver salt and adding a halogen-containing compound to the organic silver salt to convert a part of silver of the organic silver salt into photosensitive silver halide and a method of adding a silver-providing compound and a halogen-providing compound to a solution of gelatin or another polymer to form photosensitive silver halide grains and mixing the grains with an organic silver salt. The latter method is preferred in the practice of the invention. The photosensitive silver halide should preferably have a smaller mean grain size for the purpose of minimizing white turbidity after image formation. Specifically, the grain size is preferably up to 0.20  $\mu\text{m}$ , more preferably 0.01  $\mu\text{m}$  to 0.15  $\mu\text{m}$ , most preferably 0.02  $\mu\text{m}$  to 0.12  $\mu\text{m}$ . The term grain size designates the length of an edge of a silver halide grain where silver halide grains are regular grains of cubic or octahedral shape. Where silver halide grains are tabular, the grain size is the diameter of an equivalent circle having the same area as the projected area of a major surface of a tabular grain. Where silver halide grains are not regular, for example, in the case of spherical or rod-shaped grains, the grain size is the diameter of an equivalent sphere having the same volume as a grain.

**[0045]** The shape of silver halide grains may be cubic, octahedral, tabular, spherical, rod-like and potato-like, with cubic and tabular grains being preferred in the practice of the invention. Where tabular silver halide grains are used, they should preferably have an average aspect ratio of from 100:1 to 2:1, more preferably from 50:1 to 3:1. Silver halide grains having rounded corners are also preferably used. No particular limit is imposed on the face indices (Miller indices) of an outer surface of photo-sensitive silver halide grains. Preferably silver halide grains have a high proportion of {100} face featuring high spectral sensitization efficiency upon adsorption of a spectral sensitizing dye. The proportion of {100} face is preferably at least 50%, more preferably at least 65%, most preferably at least 80%. Note that the proportion of Miller index {100} face can be determined by the method described in T. Tani, J. Imaging Sci., 29, 165 (1985), utilizing the adsorption dependency of {111} face and {100} face upon adsorption of a sensitizing dye.

**[0046]** The halogen composition of photosensitive silver halide is not critical and may be any of silver chloride, silver chlorobromide, silver bromide, silver iodobromide, silver iodochlorobromide, and silver iodide. Silver bromide or silver iodobromide is preferred in the practice of the invention. Most preferred is silver iodobromide preferably having a silver iodide content of 0.1 to 40 mol%, especially 0.1 to 20 mol%. The halogen composition in grains may have a uniform distribution or a non-uniform distribution wherein the halogen concentration changes in a stepped or continuous manner. Preferred are silver iodobromide grains having a higher silver iodide content in the interior. Silver halide grains of the core/shell structure are also useful. Such core/shell grains preferably have a multilayer structure of 2 to 5 layers, more preferably 2 to 4 layers.

**[0047]** Preferably the photosensitive silver halide grains used herein contain at least one complex of a metal selected from the group consisting of rhodium, rhenium, ruthenium, osmium, iridium, cobalt, mercury, and iron. The metal complexes may be used alone or in admixture of two or more complexes of a common metal or different metals. The metal complex is preferably contained in an amount of  $1 \times 10^{-9}$  to  $1 \times 10^{-2}$  mol, more preferably  $1 \times 10^{-8}$  to  $1 \times 10^{-3}$  mol per mol of silver. Illustrative metal complex structures are those described in JP-A 225449/1995. The cobalt and iron compounds are preferably hexacyano metal complexes while illustrative, non-limiting examples include ferricyanate, ferrocyanate, and hexacyanocobaltate ions. The distribution of the metal complex in silver halide grains is not critical. That is, the metal complex may be contained in silver halide grains to form a uniform phase or at a high concentration in either the core or the shell.

**[0048]** Photosensitive silver halide grains may be desalted by any of well-known water washing methods such as noodle and flocculation methods although silver halide grains may be either desalted or not according to the invention.

**[0049]** The photosensitive silver halide grains used herein should preferably be chemically sensitized. Preferred chemical sensitization methods are sulfur, selenium, and tellurium sensitization methods which are well known in the art. Also useful are a noble metal sensitization method using compounds of gold, platinum, palladium, and iridium and a reduction sensitization method. In the sulfur, selenium, and tellurium sensitization methods, any of compounds well known for the purpose may be used. For example, the compounds described in JP-A 128768/1995 are useful. Exemplary tellurium sensitizing agents include diacyltellurides, bis(oxycarbonyl)tellurides, bis(carbamoyl)tellurides, bis(oxycarbonyl)ditellurides, bis(carbamoyl)ditellurides, compounds having a  $P=Te$  bond, tellurocarboxylic salts, Te-organyltellurocarboxylic esters, di(poly)tellurides, tellurides, telluroles, telluroacetals, tellurosulfonates, compounds having a  $P-Te$  bond, Te-containing heterocycles, tellurocarbonyl compounds, inorganic tellurium compounds, and colloidal tellurium. The preferred compounds used in the noble metal sensitization method include chloroauric acid, potassium chloroaurate, potassium aurithiocyanate, gold sulfide, and gold selenide as well as the compounds described in USP 2,448,060 and BP 618,061. Illustrative examples of the compound used in the reduction sensitization method include ascorbic acid, thiourea dioxide, stannous chloride, aminoiminomethanesulfinic acid, hydrazine derivatives, borane compounds, silane compounds, and polyamine compounds. Reduction sensitization may also be accomplished by ripening the emulsion while maintaining it at pH 7 or higher or at pAg 8.3 or lower. Reduction sensitization may also be accomplished by introducing a single addition portion of silver ion during grain formation.

**[0050]** According to the invention, the photosensitive silver halide is preferably used in an amount of 0.01 to 0.5 mol, more preferably 0.02 to 0.3 mol, most preferably 0.03 to 0.25 mol per mol of the organic silver salt. With respect to a method and conditions of admixing the separately prepared photosensitive silver halide and organic silver salt, there may be used a method of admixing the separately prepared photosensitive silver halide and organic silver salt in a high speed agitator, ball mill, sand mill, colloidal mill, vibrating mill or homogenizer or a method of preparing an organic silver salt by adding the already prepared photosensitive silver halide at any timing during preparation of an organic silver salt. Any desired mixing method may be used insofar as the benefits of the invention are fully achievable.

**[0051]** One of the preferred methods for preparing the silver halide according to the invention is a so-called halidation method of partially halogenating the silver of an organic silver salt with an organic or inorganic halide. Any of organic halides which can react with organic silver salts to form silver halides may be used. Exemplary organic halides are N-halogenoimides (e.g., N-bromosuccinimide), halogenated quaternary nitrogen compounds (e.g., tetrabutylammonium bromide), and aggregates of a halogenated quaternary nitrogen salt and a molecular halogen (e.g., pyridinium bromide perbromide). Any of inorganic halides which can react with organic silver salts to form silver halides may be used. Exemplary inorganic halides are alkali metal and ammonium halides (e.g., sodium chloride, lithium bromide, potassium

iodide, and ammonium bromide), alkaline earth metal halides (e.g., calcium bromide and magnesium chloride), transition metal halides (e.g., ferric chloride and cupric bromide), metal complexes having a halogen ligand (e.g., sodium iridate bromide and ammonium rhodate chloride), and molecular halogens (e.g., bromine, chlorine and iodine). A mixture of organic and inorganic halides may also be used.

**[0052]** The amount of the halide added for the halidation purpose is preferably 1 mmol to 500 mmol, especially 10 mmol to 250 mmol of halogen atom per mol of the organic silver salt.

#### Sensitizing dye

**[0053]** A sensitizing dye may be used in the practice of the invention. There may be used any of sensitizing dyes which can spectrally sensitize silver halide grains in a desired wavelength region when adsorbed to the silver halide grains. The sensitizing dyes used herein include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, styryl dyes, hemicyanine dyes, oxonol dyes, and hemioxonol dyes. Useful sensitizing dyes which can be used herein are described in Research Disclosure, Item 17643 IV-A (December 1978, page 23), *ibid.*, Item 1831 X (August 1979, page 437) and the references cited therein. It is advantageous to select a sensitizing dye having appropriate spectral sensitivity to the spectral properties of a particular light source of various laser imagers, scanners, image setters and printing plate-forming cameras.

**[0054]** Exemplary dyes for spectral sensitization to red light include compounds I-1 to I-38 described in JP-A 18726/1979, compounds I-1 to I-35 described in JP-A 75322/1994, compounds I-1 to I-34 described in JP-A 287338/1995, dyes 1 to 20 described in JP-B 39818/1980, compounds I-1 to I-37 described in JP-A 284343/1987, and compounds I-1 to I-34 described in JP-A 287338/1995 for red light sources such as He-Ne lasers, red semiconductor lasers and LED.

**[0055]** For semiconductor laser light sources in the wavelength range of 750 to 1,400 nm, spectral sensitization may be advantageously done with various known dyes including cyanine, merocyanine, styryl, hemicyanine, oxonol, hemioxonol, and xanthene dyes. Useful cyanine dyes are cyanine dyes having a basic nucleus such as a thiazoline, oxazoline, pyrroline, pyridine, oxazole, thiazole, selenazole and imidazole nucleus. Preferred examples of the useful merocyanine dye contain an acidic nucleus such as a thiohydantoin, rhodanine, oxazolidinedione, thiazolidinedione, barbituric acid, thiazolinone, malononitrile, and pyrazolone nucleus in addition to the above-mentioned basic nucleus. Among the above-mentioned cyanine and merocyanine dyes, those having an imino or carboxyl group are especially effective. A suitable choice may be made of well-known dyes as described, for example, in USP 3,761,279, 3,719,495, and 3,877,943, BP 1,466,201, 1,469,117, and 1,422,057, JP-B 10391/1991 and 52387/1994, JP-A 341432/1993, 194781/1994, and 301141/1994.

**[0056]** Especially preferred dye structures are cyanine dyes having a thioether bond-containing substituent group, examples of which are the cyanine dyes described in JP-A 58239/1987, 138638/1991, 138642/1991, 255840/1992, 72659/1993, 72661/1993, 222491/1994, 230506/1990, 258757/1994, 317868/1994, and 324425/1994, Publication of International Patent Application No. 500926/1995, and USP 5,541,054; dyes having a carboxylic group, examples of which are the dyes described in JP-A 163440/1991, 301141/1994 and USP 5,441,899; and merocyanine dyes, polynuclear merocyanine dyes, and polynuclear cyanine dyes, examples of which are the dyes described in JP-A 6329/1972, 105524/1974, 127719/1976, 80829/1977, 61517/1979, 214846/1984, 6750/1985, 159841/1988, 35109/1994, 59381/1994, 146537/1995, Publication of International Patent Application No. 50111/1993, BP 1,467,638, and USP 5,281,515.

**[0057]** Also useful in the practice of the invention are dyes capable of forming the J-band as disclosed in USP 5,510,236, 3,871,887 (Example 5), JP-A 96131/1990 and 48753/1984.

**[0058]** These sensitizing dyes may be used alone or in admixture of two or more. A combination of sensitizing dyes is often used for the purpose of supersensitization. In addition to the sensitizing dye, the emulsion may contain a dye which itself has no spectral sensitization function or a compound which does not substantially absorb visible light, but is capable of supersensitization. Useful sensitizing dyes, combinations of dyes showing supersensitization, and compounds showing supersensitization are described in Research Disclosure, Vol. 176, 17643 (December 1978), page 23, IV J and JP-B 25500/1974 and 4933/1968, JP-A 19032/1984 and 192242/1984.

**[0059]** The sensitizing dye may be added to a silver halide emulsion by directly dispersing the dye in the emulsion or by dissolving the dye in a solvent and adding the solution to the emulsion. The solvent used herein includes water, methanol, ethanol, propanol, acetone, methyl cellosolve, 2,2,3,3-tetrafluoropropanol, 2,2,2-trifluoroethanol, 3-methoxy-1-propanol, 3-methoxy-1-butanol, 1-methoxy-2-propanol, N,N-dimethylformamide and mixtures thereof.

**[0060]** Also useful are a method of dissolving a dye in a volatile organic solvent, dispersing the solution in water or hydrophilic colloid and adding the dispersion to an emulsion as disclosed in USP 3,469,987, a method of dissolving a dye in an acid and adding the solution to an emulsion or forming an aqueous solution of a dye with the aid of an acid or base and adding it to an emulsion as disclosed in JP-B 23389/1969, 27555/1969 and 22091/1982, a method of forming an aqueous solution or colloidal dispersion of a dye with the aid of a surfactant and adding it to an emulsion



as disclosed in USP 3,822,135 and 4,006,025, a method of directly dispersing a dye in hydrophilic colloid and adding the dispersion to an emulsion as disclosed in JP-A 102733/1978 and 105141/1983, and a method of dissolving a dye using a compound capable of red shift and adding the solution to an emulsion as disclosed in JP-A 74624/1976. It is also acceptable to apply ultrasonic waves to form a solution.

**[0061]** The time when the sensitizing dye is added to the silver halide emulsion according to the invention is at any step of an emulsion preparing process which has been ascertained effective. The sensitizing dye may be added to the emulsion at any stage or step before the emulsion is coated, for example, at a stage prior to the silver halide grain forming step and/or desalting step, during the desalting step and/or a stage from desalting to the start of chemical ripening as disclosed in USP 2,735,766, 3,628,960, 4,183,756, and 4,225,666, JP-A 184142/1983 and 196749/1985, and a stage immediately before or during chemical ripening and a stage from chemical ripening to emulsion coating as disclosed in JP-A 113920/1983. Also as disclosed in USP 4,225,666 and JP-A 7629/1983, an identical compound may be added alone or in combination with a compound of different structure in divided portions, for example, in divided portions during a grain forming step and during a chemical ripening step or after the completion of chemical ripening, or before or during chemical ripening and after the completion thereof. The type of compound or the combination of compounds to be added in divided portions may be changed.

**[0062]** The amount of the sensitizing dye used may be an appropriate amount complying with sensitivity and fog although the preferred amount is about  $10^{-6}$  to 1 mol, more preferably  $10^{-4}$  to  $10^{-1}$  mol per mol of the silver halide in the photosensitive layer.

#### Toner

**[0063]** A higher optical density is sometimes achieved when an additive known as a "toner" for improving images is contained. The toner is also sometimes advantageous in forming black silver images. The toner is preferably used in an amount of 0.1 to 50 mol%, especially 0.5 to 20 mol% per mol of silver on the image forming layer-bearing side. The toner may take the form of a precursor which is modified so as to exert its effective function only at the time of development.

**[0064]** For photothermographic imaging elements using organic silver salts, a wide range of toners are disclosed, for example, in JP-A 6077/1971, 10282/1972, 5019/1974, 5020/1974, 91215/1974, 2524/1975, 32927/1975, 67132/1975, 67641/1975, 114217/1975, 3223/1976, 27923/1976, 14788/1977, 99813/1977, 1020/1978, 76020/1978, 156524/1979, 156525/1979, 183642/1986, and 56848/1992, JP-B 10727/1974 and 20333/1979, USP 3,080,254, 3,446,648, 3,782,941, 4,123,282, 4,510,236, BP 1,380,795, and Belgian Patent No. 841,910. Examples of the toner include phthalimide and N-hydroxyphthalimide; cyclic imides such as succinimide, pyrazolin-5-one, quinazolinone, 3-phenyl-2-pyrazolin-5-one, 1-phenylurazol, quinazoline and 2,4-thiazolizinedione; naphthalimides such as N-hydroxy-1,8-naphthalimide; cobalt complexes such as cobaltic hexamine trifluoroacetate; mercaptans as exemplified by 3-mercapto-1,2,4-triazole, 2,4-dimercapto-pyrimidine, 3-mercapto-4,5-diphenyl-1,2,4-triazole, and 2,5-dimercapto-1,3,4-thiadiazole; N-(aminomethyl)aryldicarboxyimides such as (N,N-dimethylaminomethyl)phthalimide and N,N-(dimethylaminomethyl)-naphthalene-2,3-dicarboxyimide; blocked pyrazoles, isothiuronium derivatives and certain photo-bleach agents such as N,N'-hexamethylenebis(1-carbamoyl-3,5-dimethylpyrazole), 1,8-(3,6-diazaoctane)bis(isothiuronium-trifluoroacetate) and 2-tribromomethylsulfonyl-benzothiazole; 3-ethyl-5-((3-ethyl-2-benzothiazolinyldene)-1-methylethylidene)-2-thio-2,4-oxazolidinedione; phthalazinone, phthalazinone derivatives or metal salts, or derivatives such as 4-(1-naphthyl)phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone and 2,3-dihydro-1,4-phthalazinedione; phthalazine, phthalazine derivatives or metal salts, or derivatives such as 4-(1-naphthyl)phthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydro-1,4-phthalazinedione; combinations of phthalazinones with phthalic acid derivatives (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid and tetrachlorophthalic anhydride); phthalazine, phthalazine derivatives or metal salts such as 4-(1-naphthyl)phthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine; combinations of phthalazine with phthalic acid derivatives (e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid and tetrachlorophthalic anhydride); quinazolinone, benzoxazine or naphthoxazine derivatives; rhodium complexes which function not only as a tone regulating agent, but also as a source of halide ion for generating silver halide in situ, for example, ammonium hexachlororhodate (III), rhodium bromide, rhodium nitrate and potassium hexachlororhodate (III); inorganic peroxides and persulfates such as ammonium peroxide disulfide and hydrogen peroxide; benzoxazine-2,4-diones such as 1,3-benzoxazine-2,4-dione, 8-methyl-1,3-benzoxazine-2,4-dione, and 6-nitro-1,3-benzoxazine-2,4-dione; pyrimidine and asym- triazines such as 2,4-dihydroxypyrimidine and 2-hydroxy-4-aminopyrimidine; azauracil and tetraazapentalene derivatives such as 3,6-dimercapto-1,4-diphenyl-1H,4H-2,3a,5,6a-tetraazapentalene, and 1,4-di(o-chlorophenyl)-3,6-dimercapto-1H,4H-2,3a,5,6a-tetraazapentalene.

**[0065]** The toner may be added in any desired form, for example, as a solution, powder and solid particle dispersion. The solid particle dispersion of the toner is prepared by well-known finely dividing means such as ball mills, vibrating ball mills, sand mills, colloid mills, jet mills, and roller mills. Dispersing aids may be used in preparing the solid particle

dispersion.

#### Antifoggant

**[0066]** With antifoggants, stabilizers and stabilizer precursors, the silver halide emulsion and/or organic silver salt according to the invention can be further protected against formation of additional fog and stabilized against lowering of sensitivity during shelf storage. Suitable antifoggants, stabilizers and stabilizer precursors which can be used alone or in combination include thiazonium salts as described in USP 2,131,038 and 2,694,716, azaindenes as described in USP 2,886,437 and 2,444,605, mercury salts as described in USP 2,728,663, urazoles as described in USP 3,287,135, sulfocatechols as described in USP 3,235,652, oximes, nitrons and nitroindazoles as described in BP 623,448, polyvalent metal salts as described in USP 2,839,405, thiuronium salts as described in USP 3,220,839, palladium, platinum and gold salts as described in USP 2,566,263 and 2,597,915, halogen-substituted organic compounds as described in USP 4,108,665 and 4,442,202, triazines as described in USP 4,128,557, 4,137,079, 4,138,365 and 4,459,350, and phosphorus compounds as described in USP 4,411,985.

**[0067]** Preferred antifoggants are organic halides, for example, the compounds described in JP-A 119624/1975, 120328/1975, 121332/1976, 58022/1979, 70543/1981, 99335/1981, 90842/1984, 129642/1986, 129845/1987, 208191/1994, 5621/1995, 2781/1995, 15809/1996, USP 5,340,712, 5,369,000, and 5,464,737.

**[0068]** The antifoggant may be added in any desired form such as solution, powder or solid particle dispersion. The solid particle dispersion of the antifoggant may be prepared by well-known comminuting means such as ball mills, vibrating ball mills, sand mills, colloidal mills, jet mills, and roller mills. Dispersing aids may be used for facilitating dispersion.

**[0069]** It is sometimes advantageous to add a mercury (II) salt to an emulsion layer as an antifoggant though not necessary in the practice of the invention. Mercury (II) salts preferred to this end are mercury acetate and mercury bromide. The mercury (II) salt is preferably added in an amount of 1 nmol to 1 mmol, more preferably 10 nmol to 100  $\mu$ mol per mol of silver coated.

**[0070]** Still further, the photothermographic imaging element of the invention may contain a benzoic acid type compound for the purposes of increasing sensitivity and restraining fog. Any of benzoic acid type compounds may be used although examples of the preferred structure are described in USP 4,784,939 and 4,152,160, Japanese Patent Application Nos. 98051/1996, 151241/1996, and 151242/1996. The benzoic acid type compound may be added to any site in the imaging element, preferably to a layer on the same side as the photosensitive layer serving as the image forming layer, and more preferably an organic silver salt-containing layer. The benzoic acid type compound may be added at any step in the preparation of a coating solution. Where it is contained in an organic silver salt-containing layer, it may be added at any step from the preparation of the organic silver salt to the preparation of a coating solution, preferably after the preparation of the organic silver salt and immediately before coating. The benzoic acid type compound may be added in any desired form including powder, solution and fine particle dispersion. Alternatively, it may be added in a solution form after mixing it with other additives such as a sensitizing dye, reducing agent and toner. The benzoic acid type compound may be added in any desired amount, preferably 1  $\mu$ mol to 2 mol, more preferably 1 mmol to 0.5 mol per mol of silver.

**[0071]** In the imaging element of the invention, mercapto, disulfide and thion compounds may be added for the purposes of retarding or accelerating development to control development, improving spectral sensitization efficiency, and improving storage stability before and after development.

**[0072]** Where mercapto compounds are used herein, any structure is acceptable. Preferred are structures represented by Ar-S-M and Ar-S-S-Ar wherein M is a hydrogen atom or alkali metal atom, and Ar is an aromatic ring or fused aromatic ring having at least one nitrogen, sulfur, oxygen, selenium or tellurium atom. Preferred hetero-aromatic rings are benzimidazole, naphthimidazole, benzothiazole, naphthothiazole, benzoxazole, naphthoxazole, benzoxelenazole, benzotellurazole, imidazole, oxazole, pyrazole, triazole, thiadiazole, tetrazole, triazine, pyrimidine, pyridazine, pyrazine, pyridine, purine, quinoline and quinazolinone rings. These hetero-aromatic rings may have a substituent selected from the group consisting of halogen (e.g., Br and Cl), hydroxy, amino, carboxy, alkyl groups (having at least 1 carbon atom, preferably 1 to 4 carbon atoms), and alkoxy groups (having at least 1 carbon atom, preferably 1 to 4 carbon atoms). Illustrative, non-limiting examples of the mercapto-substituted hetero-aromatic compound include 2-mercaptobenzimidazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 2-mercapto-5-methylbenzimidazole, 6-ethoxy-2-mercaptobenzothiazole, 2,2'-dithiobis(benzothiazole), 3-mercapto-1,2,4-triazole, 4,5-diphenyl-2-imidazolethiol, 2-mercaptoimidazole, 1-ethyl-2-mercaptobenzimidazole, 2-mercaptoquinoline, 8-mercaptopurine, 2-mercapto-4(3H)quinazolinone, 7-trifluoromethyl-4-quinolinethiol, 2,3,5,6-tetrachloro-4-pyridinethiol, 4-amino-6-hydroxy-2-mercaptopyrimidine monohydrate, 2-amino-5-mercapto-1,3,4-3-amino-5-mercapto-1,2,4-triazole, 4-hydroxy-2-mercaptopyrimidine, 2-mercaptopyrimidine, 4,6-diamino-2-mercaptopyrimidine, 2-mercapto-4-methylpyrimidine hydrochloride, 3-mercapto-5-phenyl-1,2,4-triazole, and 2-mercapto-4-phenyloxazole.

**[0073]** These mercapto compounds are preferably added to the emulsion layer (serving as the image forming layer)

in amounts of 0.001 to 1.0 mol, more preferably 0.01 to 0.3 mol per mol of silver.

[0074] In the photosensitive layer, polyhydric alcohols (e.g., glycerin and diols as described in USP 2,960,404), fatty acids and esters thereof as described in USP 2,588,765 and 3,121,060, and silicone resins as described in BP 955,061 may be added as a plasticizer and lubricant.

#### Contrast enhancer

[0075] In the imaging element of the invention, contrast enhancers may be used for forming ultrahigh contrast images. Included are hydrazine derivatives as described in USP 5,464,738, 5,496,695, 5,512,411, 5,536,622, Japanese Patent Application Nos. 228627/1995, 215822/1996, 130842/1996, 148113/1996, 156378/1996, 148111/1996, and 148116/1996; compounds having a quaternary nitrogen atom as described in Japanese Patent Application No. 83566/1996, and acrylonitrile compounds as described in USP 5,545,515. Illustrative examples are compounds 1 to 10 in USP 5,464,738, compounds H-1 to H-28 in USP 5,496,695, compounds I-1 to I-86 in Japanese Patent Application No. 215822/1996, compounds H-1 to H-62 in 130842/1996, compounds I-1 to I-21 in 148113/1996, compounds 1 to 50 in 148111/1996, compounds 1 to 40 in 148116/1996, and compounds P-1 to P-26 and T-1 to T-18 in 83566/1996, and compounds CN-1 to CN-13 in USP 5,545,515.

[0076] A contrast enhancement accelerator may be used along with the contrast enhancer for the purpose of forming ultrahigh contrast images. Exemplary are the amine compounds described in USP 5,545,505, specifically AM-1 to AM-5; hydroxamic acid type compounds described in USP 5,545,507, specifically HA-1 to HA-11, acrylonitriles described in USP 5,545,507, specifically CN-1 to CN-13, hydrazine compounds described in USP 5,558,983, specifically CA-1 to CA-6, onium salts described in Japanese Patent Application No. 132836/1996, specifically A-1 to A-42, B-1 to B-27, and C-1 to C-14.

[0077] With respect to the synthesis method, addition method and addition amount of these contrast enhancers and contrast enhancement accelerators, reference should be made to the above-referred patents.

#### Protective layer

[0078] A surface protective layer may be provided in the imaging element according to the present invention for the purpose of preventing sticking of an image forming layer.

[0079] The surface protective layer is based on a binder which may be any desired polymer, although the layer preferably contains 100 mg/m<sup>2</sup> to 5 g/m<sup>2</sup> of a polymer having a carboxylic acid residue. The polymers having a carboxylic acid residue include natural polymers (e.g., gelatin and alginic acid), modified natural polymers (e.g., carboxymethyl cellulose and phthalated gelatin), and synthetic polymers (e.g., polymethacrylate, polyacrylate, polyalkyl methacrylate/acrylate copolymers, and polystyrene/polymethacrylate copolymers). The content of the carboxylic acid residue is preferably 10 mmol to 1.4 mol per 100 grams of the polymer. The carboxylic acid residue may form a salt with an alkali metal ion, alkaline earth metal ion or organic cation.

[0080] In the surface protective layer, any desired anti-sticking anti-sticking material may be used. Examples of the material include wax, silica particles, styrene-containing elastomeric block copolymers (e.g., styrene-butadiene-styrene and styrene-isoprene-styrene), cellulose acetate, cellulose acetate butyrate, cellulose propionate and mixtures thereof. Crosslinking agents for crosslinking, surfactants for ease of application, and other addenda are optionally added to the surface protective layer.

[0081] In the image forming layer or a protective layer therefor according to the invention, there may be used light absorbing substances and filter dyes as described in USP 3,253,921, 2,274,782, 2,527,583, and 2,956,879. The dyes may be mordanted as described in USP 3,282,699. The filter dyes are used in such amounts that the layer may have an absorbance of 0.1 to 3, especially 0.2 to 1.5 at the exposure wavelength.

[0082] In the image forming layer or a protective layer therefor according to the invention, there may be used matte agents, for example, starch, titanium dioxide, zinc oxide, and silica as well as polymer beads including beads of the type described in USP 2,992,101 and 2,701,245. The image forming or protective layer surface may have any degree of matte insofar as no star dust failures occur although a Bekk smoothness of 200 to 10,000 seconds, especially 300 to 10,000 seconds is preferred.

[0083] The thermographic photographic emulsion used in the photothermographic imaging material according to the one preferred embodiment of the invention is contained in one or more layers on a support. In the event of single layer construction, it should contain an organic silver salt, silver halide, developing agent, and binder, and other optional additives such as a toner, coating aid and other auxiliary agents. In the event of two-layer construction, a first emulsion layer which is generally a layer disposed adjacent to the support should contain an organic silver salt and silver halide and a second emulsion layer or both the layers contain other components. Also envisioned herein is a two-layer construction consisting of a single emulsion layer containing all the components and a protective topcoat. In the case of multi-color sensitive photothermographic material, a combination of such two layers may be employed for each color.

Also a single layer may contain all necessary components as described in USP 4,708,928. In the case of multi-dye, multi-color sensitive photothermographic material, emulsion (or photosensitive) layers are distinctly supported by providing a functional or non-functional barrier layer therebetween as described in USP 4,460,681.

**[0084]** In the photosensitive layer, a variety of dyes and pigments may be used from the standpoints of improving tone and preventing irradiation. Any desired dyes and pigments may be used in the invention. Useful pigments and dyes include those described in Colour Index and both organic and inorganic, for example, pyrazoloazole dyes, anthraquinone dyes, azo dyes, azomethine dyes, oxonol dyes, carbocyanine dyes, styryl dyes, triphenylmethane dyes, indoaniline dyes, indophenol dyes, and phthalocyanine dyes. The preferred dyes used herein include anthraquinone dyes (e.g., Compounds 1 to 9 described in JP-A 341441/1993 and Compounds 3-6 to 3-18 and 3-23 to 3-38 described in JP-A 165147/1993), azomethine dyes (e.g., Compounds 17 to 47 described in JP-A 341441/1993), indoaniline dyes (e.g., Compounds 11 to 19 described in JP-A 289227/1993, Compound 47 described in JP-A 341441/1993 and Compounds 2-10 to 2-11 described in JP-A 165147/1993), and azo dyes (e.g., Compounds 10 to 16 described in JP-A 341441/1993). The dyes and pigments may be added in any desired form such as solution, emulsion or solid particle dispersion or in a form mordanted with polymeric mordants. The amounts of these compounds used are determined in accordance with the desired absorption although the compounds are generally used in amounts of 1 µg to 1 g per square meter of the imaging element.

**[0085]** In the practice of the invention, an antihalation layer may be disposed on the side of the photosensitive layer remote from the light source. The antihalation layer preferably has a maximum absorbance of 0.3 to 2 in the desired wavelength range, more preferably an absorbance of 0.5 to 2 at the exposure wavelength, and an absorbance of 0.001 to less than 0.5 in the visible region after processing, and is also preferably a layer having an optical density of 0.001 to less than 0.3.

**[0086]** Where an antihalation dye is used in the invention, it may be selected from various compounds insofar as it has the desired absorption in the wavelength range, is sufficiently low absorptive in the visible region after processing, and provides the antihalation layer with the preferred absorbance profile. Exemplary antihalation dyes are given below though the dyes are not limited thereto. Useful dyes which are used alone are described in JP-A 56458/1984, 216140/1990, 13295/1995, 11432/1995, USP 5,380,635, JP-A 68539/1990, page 13, lower-left column, line 1 to page 14, lower-left column, line 9, and JP-A 24539/1991, page 14, lower-left column to page 16, lower-right column. It is further preferable in the practice of the invention to use a dye which will decolorize during processing. Illustrative, non-limiting, examples of decolorizable dyes are disclosed in JP-A 139136/1977, 132334/1978, 501480/1981, 16060/1982, 68831/1982, 101835/1982, 182436/1984, 36145/1995, 199409/1995, JP-B 33692/1973, 16648/1975, 41734/1990, USP 4,088,497, 4,283,487, 4,548,896, and 5,187,049.

**[0087]** In one preferred embodiment, the photothermographic element of the invention is a one-side photosensitive element having at least one photosensitive layer containing a silver halide emulsion on one side and a back layer on the other side of the support.

**[0088]** In the practice of the invention, a matte agent may be added to the imaging element for improving feed efficiency. The matte agents used herein are generally microparticulate water-insoluble organic or inorganic compounds. There may be used any desired one of matte agents, for example, well-known matte agents including organic matte agents as described in USP 1,939,213, 2,701,245, 2,322,037, 3,262,782, 3,539,344, and 3,767,448 and inorganic matte agents as described in USP 1,260,772, 2,192,241, 3,257,206, 3,370,951, 3,523,022, and 3,769,020. Illustrative examples of the organic compound which can be used as the matte agent are given below; exemplary water-dispersible vinyl polymers include polymethyl acrylate, polymethyl methacrylate, polyacrylonitrile, acrylonitrile- $\alpha$ -methylstyrene copolymers, polystyrene, styrene-divinylbenzene copolymers, polyvinyl acetate, polyethylene carbonate, and polytetrafluoroethylene; exemplary cellulose derivatives include methyl cellulose, cellulose acetate, and cellulose acetate propionate; exemplary starch derivatives include carboxystarch, carboxynitrophenyl starch, urea-formaldehydestarch reaction products, gelatin hardened with well-known curing agents, and hardened gelatin which has been coacervation hardened into microcapsulated hollow particles. Preferred examples of the inorganic compound which can be used as the matte agent include silicon dioxide, titanium dioxide, magnesium dioxide, aluminum oxide, barium sulfate, calcium carbonate, silver chloride and silver bromide desensitized by a well-known method, glass, and diatomaceous earth. The aforementioned matte agents may be used as a mixture of substances of different types if necessary. The size and shape of the matte agent are not critical. The matte agent of any particle size may be used although matte agents having a particle size of 0.1 µm to 30 µm are preferably used in the practice of the invention. The particle size distribution of the matte agent may be either narrow or wide. Nevertheless, since the haze and surface luster of photosensitive material are largely affected by the matte agent, it is preferred to adjust the particle size, shape and particle size distribution of a matte agent as desired during preparation of the matte agent or by mixing plural matte agents.

**[0089]** In the practice of the invention, the back layer should preferably have a degree of matte as expressed by a Bekk smoothness of 10 to 250 seconds, more preferably 50 to 180 seconds.

**[0090]** In the imaging element of the invention, the matte agent is preferably contained in an outermost surface layer, a layer functioning as an outermost surface layer, a layer close to the outer surface or a layer functioning as a so-called

protective layer.

[0091] In the practice of the invention, the binder used in the back layer is preferably transparent or translucent and generally colorless. Exemplary binders are naturally occurring polymers, synthetic resins, polymers and copolymers, and other film-forming media, for example, gelatin, gum arabic, poly(vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, poly(vinyl pyrrolidone), casein, starch, poly(acrylic acid), poly(methyl methacrylate), polyvinyl chloride, poly(methacrylic acid), copoly(styrene-maleic anhydride), copoly(styrene-acrylonitrile), copoly(styrene-butadiene), polyvinyl acetals (e.g., polyvinyl formal and polyvinyl butyral), polyesters, polyurethanes, phenoxy resins, poly(vinylidene chloride), polyepoxides, polycarbonates, poly(vinyl acetate), cellulose esters, and polyamides. The binder may be dispersed in water, organic solvent or emulsion to form a dispersion which is coated to form a layer.

[0092] The back layer preferably exhibits a maximum absorbance of 0.3 to 2, more preferably 0.5 to 2 in the predetermined wavelength range and an absorbance of 0.001 to less than 0.5, more preferably 0.001 to less than 0.3 in the visible range after processing. Further preferably, the back layer has an optical density of 0.001 to less than 0.3. Examples of the antihalation dye used in the back layer are the same as previously described for the antihalation layer.

[0093] A backside resistive heating layer as described in USP 4,460,681 and 4,374,921 may be used in a photo-thermographic imaging system according to the present invention.

[0094] According to the invention, a hardener may be used in various layers including an image forming layer, protective layer, and back layer. Examples of the hardener include polyisocyanates as described in USP 4,281,060 and JP-A 208193/1994, epoxy compounds as described in USP 4,791,042, and vinyl sulfones as described in JP-A 89048/1987.

[0095] A surfactant may be used for the purposes of improving coating and electric charging properties. The surfactants used herein may be nonionic, anionic, cationic and fluorinated ones. Examples include fluorinated polymer surfactants as described in JP-A 170950/1987 and USP 5,380,644, fluorinated surfactants as described in JP-A 244945/1985 and 188135/1988, polysiloxane surfactants as described in USP 3,885,965, and polyalkylene oxide and anionic surfactants as described in JP-A 301140/1994.

[0096] Examples of the solvent used herein are described in "New Solvent Pocket Book," Ohm K.K., 1994, though not limited thereto. The solvent used herein should preferably have a boiling point of 40 to 180°C. Exemplary solvents include hexane, cyclohexane, toluene, methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, ethyl acetate, 1,1,1-trichloroethane, tetrahydrofuran, triethylamine, thiophene, trifluoroethanol, perfluoropentane, xylene, n-butanol, phenol, methyl isobutyl ketone, cyclohexanone, butyl acetate, diethyl carbonate, chlorobenzene, dibutyl ether, anisole, ethylene glycol diethyl ether, N,N-dimethylformamide, morpholine, propanesultone, perfluorotributylamine, and water.

#### Support

[0097] According to the invention, the thermographic photographic emulsion may be coated on a variety of supports. Typical supports include polyester film, subbed polyester film, poly(ethylene terephthalate) film, polyethylene naphthalate film, cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polycarbonate film and related or resinous materials, as well as glass, paper, metals. Often used are flexible substrates, typically paper supports, specifically baryta paper and paper supports coated with partially acetylated  $\alpha$ -olefin polymers, especially polymers of  $\alpha$ -olefins having 2 to 10 carbon atoms such as polyethylene, polypropylene, and ethylene-butene copolymers. The supports are either transparent or opaque, preferably transparent.

[0098] The imaging element of the invention may have an antistatic or electroconductive layer, for example, a layer containing soluble salts (e.g., chlorides and nitrates), an evaporated metal layer, or a layer containing ionic polymers as described in USP 2,861,056 and 3,206,312 or insoluble inorganic salts as described in USP 3,428,451.

[0099] A method for producing color images using the photothermographic material of the invention is as described in JP-A 13295/1995, page 10, left column, line 43 to page 11, left column, line 40. Stabilizers for color dye images are exemplified in BP 1,326,889, USP 3,432,300, 3,698,909, 3,574,627, 3,573,050, 3,764,337, and 4,042,394.

[0100] In the practice of the invention, the photothermographic emulsion can be applied by various coating procedures including dip coating, air knife coating, flow coating, and extrusion coating using a hopper of the type described in USP 2,681,294. The coating techniques recommended in the invention are described in Stephan F. Kistler and Peter M. Schweizer, LIQUID FILM COATING, CHAPMA & HALL, 1997, pp. 399-734, and more preferably, extrusion coating, slide coating, and curtain coating. Of the coating machines used in these coating techniques, exemplary extrusion coaters are shown in Figures 11a.1 to 11a.7 on pages 401-405, exemplary slider coaters in Figure 11b.1 on page 427, and exemplary curtain coaters in Figures 11c.1 to 11c.7 on page 464-466. If desired, two or more layers may be concurrently coated by the methods described in USP 2,761,791 and BP 837,095.

[0101] In the photothermographic element of the invention, there may be contained additional layers, for example, a dye accepting layer for accepting a mobile dye image, an opacifying layer when reflection printing is desired, a protective topcoat layer, and a primer layer well known in the photothermographic art. The photosensitive material is preferably such that only a single sheet of the photosensitive material can form an image. That is, it is preferred that

a functional layer necessary to form an image such as an image receiving layer does not constitute a separate member.

[0102] The photothermographic element of the invention may be developed by any desired method although it is generally developed by heating after imagewise exposure. The preferred developing temperature is 80 to 250°C, more preferably 100 to 140°C. The preferred developing time is 1 to 180 seconds, more preferably 10 to 90 seconds.

[0103] Any desired technique may be used for the exposure of the photothermographic element of the invention. The preferred light source for exposure is a laser, for example, a gas laser, YAG laser, dye laser or semiconductor laser. A semiconductor laser combined with a second harmonic generating device is also useful.

[0104] Upon exposure, the photothermographic element of the invention tends to generate interference fringes due to low haze. Known techniques for preventing generation of interference fringes are a technique of obliquely directing laser light to a photosensitive material as disclosed in JP-A 113548/1993 and the utilization of a multi-mode laser as disclosed in WO 95/31754. These techniques are preferably used herein.

[0105] Upon exposure of the photothermographic imaging material of the invention, exposure is preferably made by overlapping laser light so that no scanning lines are visible, as disclosed in SPIE, Vol. 169, Laser Printing 116-128 (1979), JP-A 51043/1992, and WO 95/31754.

#### EXAMPLES

[0106] Examples of the present invention are given below by way of illustration and not by way of limitation.

#### Example 1: Organic silver salt-containing liquid

##### Preparation of organic acid silver dispersion

[0107] While a mixture of 7 grams of stearic acid, 4 gram of arachidic acid, 36 grams of behenic acid, and 850 ml of distilled water was vigorously stirred at 90°C, 187 ml of 1N NaOH aqueous solution was added. Reaction was carried out for 120 minutes. After 65 ml of 1N nitric acid was added, the solution was cooled to 50°C. With more vigorous stirring, 125 ml of an aqueous solution containing 21 grams of silver nitrate was added over 100 seconds. The solution was left to stand for 20 minutes. Thereafter, the solids were separated by suction filtration and washed with water until the water filtrate reached a conductivity of 30  $\mu$ S/cm. To the thus obtained solids, 100 grams of a 10 wt% aqueous solution of hydroxypropyl methyl cellulose was added. Water was further added to a total weight of 270 grams. This was roughly dispersed in an automated mortar, obtaining a crude organic acid silver dispersion. This crude organic acid silver dispersion was dispersed in a nanomizer (manufactured by Nanomizer K.K.) under an impact pressure of 1,000 kg/cm<sup>2</sup>, obtaining an organic acid silver dispersion. The thus obtained organic acid silver dispersion contained needle grains of organic acid silver having a mean minor diameter of 0.04  $\mu$ m, a mean major diameter of 0.8  $\mu$ m and a coefficient of variation of 30%.

##### Preparation of reducing agent dispersion

[0108] A slurry was obtained by adding 850 grams of water to 100 grams of 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane and 50 grams of hydroxypropyl cellulose and thoroughly mixing them. This slurry was introduced into a vessel together with 840 grams of zirconia beads having an average diameter of 0.5 mm. A dispersing machine (1/4G Sand Grinder Mill by Imex K.K.) was operated for 5 hours for dispersion, obtaining a reducing agent dispersion.

##### Preparation of organic silver salt-containing liquid

[0109] An organic silver salt-containing liquid was prepared by thoroughly mixing amounts as shown in Table 1 of the organic acid silver dispersion, the reducing agent dispersion and LACSTAR 3307B SBR latex with amounts to give a viscosity as shown in Table 1 of a 10% aqueous solution of polyvinyl alcohol (PVA, average degree of polymerization 500, saponification 88%) and water. The organic silver salt-containing liquid thus obtained was measured for viscosity at 25°C using a liquid spectrometer RFS (Rheometrics Far East K.K.). The results are shown in Table 1.

[0110] It is noted that LACSTAR 3307B is a styrene-butadiene rubber (SBR) latex commercially available from Dai-Nippon Ink & Chemicals K.K. wherein the polymer has an equilibrium moisture content of 0.6 wt% at 25°C and RH 60% and the dispersed particles have a mean particle diameter of about 0.1 to 0.15  $\mu$ m.

##### Coating and drying of organic silver salt-containing liquid

[0111] The coater used herein is shown in FIG. 1 as comprising a backup roll 2 around which a length of support 1 is wrapped, a coating die 3 of the slide bead coating system opposed to the backup roll 2, and a vacuum chamber 5.

## EP 0 883 022 B1

While the support 1 is continuously moved around the backup roll 2, a coating solution 4 is applied from the die 3 to the support 1 so as to form a bead which is stabilized by the vacuum chamber 5. The support 1 to which the coating solution 4 has been applied is conveyed to a chilling zone A where the coating is cooled and immobilized and then to a drying zone (not shown) where the solvent is volatilized off.

5 [0112] The support used herein was a polyethylene terephthalate film of 175  $\mu\text{m}$  thick undercoated with SBR latex LACSTAR 3307B and gelatin. Using the coater, the organic silver salt-containing liquid was applied to the support at a coating rate of 100 m/min. to a coverage of 100 cc/m<sup>2</sup>. The coating was dried by blowing air of 30°C and RH 40% at a wind velocity of 20 m/sec. at the coating surface. The dry coating was examined for surface quality by counting the number of streaks formed over a coating width of 10 cm and for wind-swept unevenness by determining the difference between maximum and minimum silver contents (g/m<sup>2</sup>) of the coating. The results are shown in Table 1. For 10 both the number of streaks and the difference, smaller values indicate a better surface state.

15

20

25

30

35

40

45

50

55

Table 1

Fluid	a*	b	c*	d	e	f*	g	h	i
Organic silver salt dispersion (g)	100	100	100	100	100	67	67	80	80
Reducing agent dispersion (g)	-	-	-	-	-	33	33	20	20
SBR (g)	40	40	60	60	60	40	40	100	100
Viscosity at 0.1 s <sup>-1</sup> (mPa's)	100	1000	2000	10000	5000	400	6000	30000	50000
Viscosity at 1000 s <sup>-1</sup> (mPa's)	20	25	150	100	40	60	30	80	100
Streaks (/10 cm)	0	0	3.2	0.04	0	0.05	0	0.02	0.10
Silver content difference (g/m <sup>2</sup> )	1.2	0.05	1.0	0.01	0.02	1.4	0.02	0.02	0.03

\*Comparison Invention

[0113] It is evident that samples within the scope of the invention are satisfactory in surface quality.



Example 2: Thermographic imaging elementSilver halide grains

[0114] In 700 ml of water were dissolved 22 grams of phthalated gelatin and 30 mg of potassium bromide. The solution was adjusted to pH 5.0 at a temperature of 35°C. To the solution, 159 ml of an aqueous solution containing 18.6 grams of silver nitrate and 0.9 gram of ammonium nitrate and an aqueous solution containing potassium bromide and potassium iodide in a molar ratio of 92:8 were added over 10 minutes by the controlled double jet method while maintaining the solution at pAg 7.7. Then, 476 ml of an aqueous solution containing 55.4 grams of silver nitrate and 2 grams of ammonium nitrate and an aqueous solution containing 10 µmol/liter of dipotassium hexachloroiridate and 1 mol/liter of potassium bromide were added over 30 minutes by the controlled double jet method while maintaining the solution at pAg 7.7. After 1 gram of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added, the pH of the solution was lowered to cause flocculation and sedimentation for desalting. The solution was adjusted to pH 5.9 and pAg 8.2 by adding 0.1 gram of phenoxyethanol. There were obtained cubic grains of silver iodobromide having an iodide content of 8 mol% in the core and 2 mol% on the average, a mean grain size of 0.05 µm, a coefficient of variation of the projected area of 8%, and a (100) face proportion of 85%.

[0115] The thus obtained silver halide grains were heated at 60°C, to which 85 µmol of sodium thiosulfate, 11 µmol of 2,3,4,5,6-pentafluorophenyldiphenylphosphine selenide, 15 µmol of Tellurium Compound, 3 µmol of chloroauric acid, and 270 µmol of thiocyanic acid were added per mol of silver. The emulsion was ripened for 120 minutes and then quenched to 40°C. Then, 100 µmol of Dye and 500 µmol of 2-mercapto-5-methylbenzimidazole were added to the emulsion, which was quenched to 30°C, completing the preparation of a silver halide emulsion.

Organic polyhalogenated compound dispersion

[0116] A slurry was obtained by adding 940 grams of water to 50 grams of tribromomethylphenylsulfone and 10 grams of hydroxypropyl cellulose and thoroughly mixing them. This slurry was introduced into a vessel together with 840 grams of zirconia beads having an average diameter of 0.5 mm. A dispersing machine (1/4G Sand Grinder Mill by Imex K.K.) was operated for 5 hours for dispersion, obtaining an organic polyhalogenated compound dispersion.

Emulsion layer coating solution

[0117] An emulsion layer coating solution was prepared by thoroughly mixing 100 grams of the organic acid silver dispersion, 20 grams of the reducing agent dispersion, both obtained in Example 1, 15 grams of the organic polyhalogenated compound dispersion prepared above, 20 grams of LACSTAR 3307B SBR latex, 10 grams of the silver halide emulsion prepared above, and an amount to give a viscosity as shown in Table 2 of water.

Emulsion surface protective layer coating solution

[0118] A coating solution for the surface protective layer was prepared by adding 860 mg of a sodium salt of di(2-ethylhexyl) sulfosuccinate, 0.8 grams of microparticulate poly(methyl methacrylate) having a mean particle size of 2.5 µm, 5.3 g of phthalazine, 10 g of 4-methylphthalic acid, 4.2 g of aluminum sulfate, and 0.8 g of chromium (III) potassium sulfate dodecahydrate to 100 grams of inert gelatin, and further adding water to a total volume of 1600 ml.

Back layer coating solution

[0119] A base solution was prepared by dispersing 10 grams of a salt of N,N,N,N-tetraethylguanidine and 4-carboxysulfonylphenylsulfone in a molar ratio of 1:2 as a solid base in 10 grams of polyvinyl alcohol and 88 grams of water in a dispersing machine (1/16G Sand Grinder Mill by Imex K.K.).

[0120] An organic solvent phase was prepared by mixing and dissolving 2.1 grams of a Basic Dye Precursor, 7.9 grams of an Acidic Substance, 0.1 gram of a Dyestuff, and 10 grams of ethyl acetate. This organic solvent phase was mixed with an aqueous solution phase consisting of 10 grams of polyvinyl alcohol and 80 grams of water, emulsified and dispersed at room temperature, obtaining a dyestuff solution having a mean particle size of 2.5 µm.

[0121] A back surface coating solution was prepared by mixing 39 grams of the base solution, 26 grams of the dyestuff solution, and 36 grams of a 10 wt% aqueous solution of polyvinyl alcohol.

Back surface protective layer coating solution

[0122] A back surface protective layer coating solution was prepared by dissolving 20 grams of gelatin, 0.6 gram of

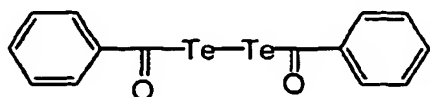
polymethyl methacrylate having a mean particle size of 7  $\mu\text{m}$ , 0.4 gram of sodium dodecylbenzenesulfonate, and 1 gram of X-22-2809 silicone compound (by Shin-Etsu Silicone K.K.) in 480 grams of water.

#### Photothermographic imaging element

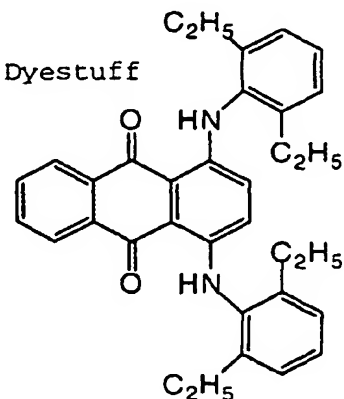
[0123] Onto the back surface of a 175- $\mu\text{m}$  thick polyethylene terephthalate support undercoated with SBR latex LACSTAR 3307B and gelatin, the back layer coating solution in an amount to provide an optical density of 0.7 at 647 nm and the back surface protective layer coating solution in an amount of 50 g/m<sup>2</sup> were concurrently applied in an overlapping manner. Then the emulsion layer coating solution was coated onto the opposite surface of the support in a silver coverage of 1.8 g/m<sup>2</sup> and dried by blowing air of 30°C and RH 40% at a wind velocity of 20 m/sec. Thereafter, the emulsion surface protective layer coating solution was coated onto the emulsion coating in a gelatin coverage of 2.2 g/m<sup>2</sup>. The thus obtained photosensitive material had a surface smoothness corresponding to a Bekk smoothness of 1,200 seconds on the emulsion side and 85 seconds on the back surface as measured by the Oken type smoothness measurement described in J. TAPPI, Paper Pulp Test No. 5.

[0124] Some of the compounds used above have the structures shown below.

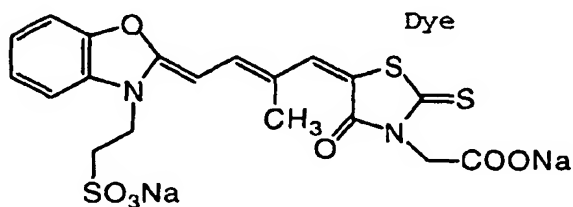
Tellurium Compound



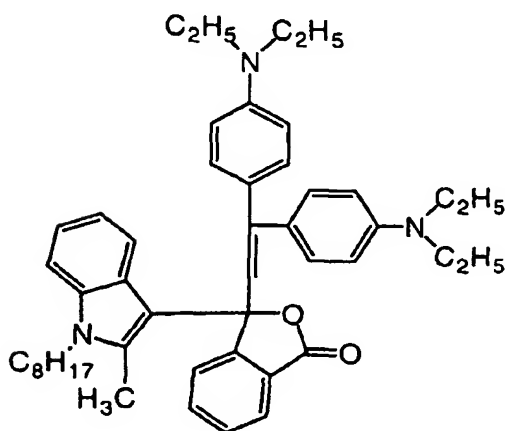
Dyestuff



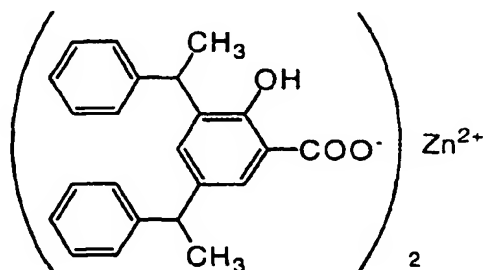
Dye



Basic Dye Precursor



Acidic Substance



#### Surface quality

[0125] The coated sample was examined for surface quality by counting the number of streaks formed over a coating

width of 10 cm and for wind-swept unevenness by determining the difference between maximum and minimum silver contents (g/m<sup>2</sup>) of the coating.

#### Photographic test

[0126] The photographic element was exposed to light at an angle of 30° relative to a normal to the material surface by means of a 647-nm Kr laser sensitometer (maximum power 500 mW) and developed by heating at 120°C for 15 seconds. The resulting image was measured for Dmin and sensitivity by means of a densitometer. The sensitivity is the reciprocal of a ratio of the exposure providing a density of Dmin + 1.0, and is expressed in a relative value based on a sensitivity of 100 for photographic element No. 3.

[0127] The results are shown in Table 2.

Table 2

Photosensitive element No.	1*	2*	3	4
Viscosity at 0.1 s <sup>-1</sup> (mPa·s)	100	10000	2000	5000
Viscosity at 1000 s <sup>-1</sup> (mPa·s)	20	120	10	40
Streaks (/10 cm)	0	0.5	0	0
Silver content difference (g/m <sup>2</sup> )	0.9	0.8	0.02	0.10
Dmin	0.25	0.22	0.12	0.10
Sensitivity	30	70	100	120

\* Comparison Invention

[0128] It is evident that samples within the scope of the invention are satisfactory in both surface quality and photographic properties.

#### Example 3

[0129] A photosensitive element sample was prepared as was photosensitive element No. 4 of Example 2 except that N-(2-methoxyphenyl)-N-formylhydrazine was added to the emulsion layer coating solution in such an amount as to give a coverage of 1 mg/m<sup>2</sup>. It was satisfactory in surface quality and photographic properties.

#### Example 4

[0130] A photosensitive element sample was prepared as was photosensitive element No. 4 of Example 2 except that the silver halide was not added to the emulsion layer coating solution, the reducing agent dispersion was replaced by an aqueous solution containing an equimolar amount of methyl 3,4-dihydroxybenzoate, and the base solution and the dyestuff solution were not added to the back surface coating solution. The sample was heated at 90°C for 5 seconds before it was examined for surface quality and color tone. It was satisfactory in both surface quality and tone.

[0131] It is thus evident that the present invention provides a thermographic imaging element having improved surface quality and a satisfactory imaging capability.

[0132] Reasonable modifications and variations are possible from the foregoing disclosure without departing from the scope of the claims.

#### Claims

1. A coating method for the preparation of a thermographic or photothermographic imaging element, comprising the step of:  
applying a liquid containing an organic silver salt and a binder and having a viscosity at 25°C of 500 mPa·s to 500,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup> and 0.1 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.
2. The method of claim 1 wherein said liquid further contains a reducing agent for silver ion.
3. The method of claim 1 or 2 wherein said organic silver salt is a silver salt of an organic carboxylic acid.
4. The method of any one of claims 1 to 3 wherein said liquid further contains a photosensitive silver halide.

## EP 0 883 022 B1

5. The method of any one of claims 1 to 4 wherein said liquid has a viscosity at 25°C of 500 mPa·s to 300,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup>.
6. The method of claim 5 wherein said liquid has a viscosity at 25°C of 1,000 mPa·s to 100,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup>.
7. The method of claim 6 wherein said liquid has a viscosity at 25°C of 1,000 mPa·s to 30,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup>.
8. The method of any one of claims 1 to 7 wherein said liquid has a viscosity at 25°C of 0.2 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.
9. The method of claim 8 wherein said liquid has a viscosity at 25°C of 1 mPa·s to 80 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.
10. The method of any one of claims 1 to 9 wherein said liquid contains fine solid particles having a size of 0.001 µm to 10 µm in a concentration of 10 to 80% by weight.
11. The method of claim 10 wherein said liquid contains fine solid particles having a size of 0.01 µm to 5 µm in a concentration of 10 to 80% by weight.
12. The method of claim 10 or 11 wherein said liquid contains the fine solid particles in a concentration of 15 to 50% by weight.
13. The method of claim 12 wherein said liquid contains the fine solid particles in a concentration of 20 to 50% by weight.
14. The method of any one of claims 1 to 13 wherein said liquid contains non-spherical fine solid particles in a concentration of 0.1 to 50% by weight.
15. The method of claim 14 wherein said liquid contains non-spherical fine solid particles in a concentration of 0.5 to 20% by weight.
16. The method of any one of claims 1 to 15 wherein said liquid contains a polymer latex in an amount of at least 50% by weight of the entire binder.
17. The method of claim 16 wherein the polymer latex has an equilibrium moisture content of up to 2% by weight at 25°C and RH 60%.
18. The method of any one of claims 1 to 17 wherein the liquid is an aqueous medium wherein water accounts for at least 30% by weight of the solvent.
19. A coating solution for forming a thermographic image forming layer, containing an organic silver salt, a reducing agent for silver ion, and a binder and having a viscosity at 25°C of 500 mPa·s to 500,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup> and 0.1 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.
20. A thermographic imaging element which has been prepared by applying a coating solution containing an organic silver salt, a reducing agent for silver ion, and a binder and having a viscosity at 25°C of 500 mPa·s to 500,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup> and 0.1 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.
21. A photothermographic imaging element which has been prepared by applying a coating solution containing an organic silver salt, a reducing agent for silver ion, a photosensitive silver halide, and a binder and having a viscosity at 25°C of 500 mPa·s to 500,000 mPa·s at a shear rate of 0.1 s<sup>-1</sup> and 0.1 mPa·s to 100 mPa·s at a shear rate of 1,000 s<sup>-1</sup>.

### Patentansprüche

1. Beschichtungsverfahren zur Herstellung eines thermographischen oder photothermographischen Bilderzeugungselements, das den Schritt

## EP 0 883 022 B1

Auftragen einer Flüssigkeit, die ein organisches Silbersalz und ein Bindemittel enthält und die bei 25°C eine Viskosität von 500 Pa·s bis 500 000 Pa·s bei einem Geschwindigkeitsgefälle von 0,1 s<sup>-1</sup> und von 0,1 m Pa·s bis 100 m Pa·s bei einem Geschwindigkeitsgefälle von 1 000 s<sup>-1</sup> hat, umfaßt.

- 5 2. Verfahren nach Anspruch 1, wobei die Flüssigkeit außerdem ein Reduktionsmittel für Silber-Ionen enthält.
3. Verfahren nach Anspruch 1 oder 2, wobei das organische Silbersalz ein Silbersalz einer organischen Carbonsäure ist.
- 10 4. Verfahren nach einem Ansprüche 1 bis 3, wobei die Flüssigkeit außerdem ein lichtempfindliches Silberhalogenid enthält.
5. Verfahren nach einem Ansprüche 1 bis 4, wobei die Flüssigkeit bei 25°C eine Viskosität von 500 mPa·s bis 300 000 mPa·s bei einem Geschwindigkeitsgefälle von 0,1 s<sup>-1</sup> hat.
- 15 6. Verfahren nach Anspruch 5, wobei die Flüssigkeit bei 25°C eine Viskosität von 1 000 mPa·s bis 100 000 mPa·s bei einem Geschwindigkeitsgefälle von 0,1 s<sup>-1</sup> hat.
- 20 7. Verfahren nach Anspruch 6, wobei die Flüssigkeit bei 25°C eine Viskosität von 1 000 mPa·s bis 30 000 mPa·s bei einem Geschwindigkeitsgefälle von 0,1 s<sup>-1</sup> hat.
8. Verfahren nach einem der Ansprüche 1 bis 7, wobei die Flüssigkeit bei 25°C eine Viskosität von 0,2 mPa·s bis 100 mPa·s bei einem Geschwindigkeitsgefälle von 1 000 s<sup>-1</sup> hat.
- 25 9. Verfahren nach Anspruch 8, wobei die Flüssigkeit bei 25°C eine Viskosität von 1 mPa·s bis 80 mPa·s bei einem Geschwindigkeitsgefälle von 1 000 s<sup>-1</sup> hat.
- 30 10. Verfahren nach einem der Ansprüche 1 bis 9, wobei die Flüssigkeit feine feste Teilchen mit einer Größe von 0,001 µm bis 10 µm in einer Konzentration von 10 bis 80 Gew.-% enthält.
11. Verfahren nach Anspruch 10, wobei die Flüssigkeit feine feste Teilchen mit einer Größe von 0,01 µm bis 5 µm in einer Konzentration von 10 bis 80 Gew.-% enthält.
- 35 12. Verfahren nach Anspruch 10 oder 11, wobei die Flüssigkeit die feinen festen Teilchen in einer Konzentration von 15 bis 50 Gew.-% enthält.
13. Verfahren nach Anspruch 12, wobei die Flüssigkeit die feinen festen Teilchen in einer Konzentration von 20 bis 50 Gew.-% enthält.
- 40 14. Verfahren nach einem der Ansprüche 1 bis 13, wobei die Flüssigkeit nicht-kugelförmige feine feste Teilchen in einer Konzentration von 0,1 bis 50 Gew.-% enthält.
15. Verfahren nach Anspruch 14, wobei die Flüssigkeit nicht-kugelförmige feine feste Teilchen in einer Konzentration von 0,5 bis 20 Gew.-% enthält.
- 45 16. Verfahren nach einem der Ansprüche 1 bis 15, wobei die Flüssigkeit einen Polymer-Latex in einer Menge von mindestens 50 Gew.-% des ganzen Bindemittels enthält.
- 50 17. Verfahren nach Anspruch 16, wobei der Polymer-Latex bei 25°C und 60 % relativer Feuchtigkeit einen Gleichgewichtsfeuchtigkeitsgehalt von bis zu 2 Gew.-% hat.
18. Verfahren nach einem der Ansprüche 1 bis 17, wobei die Flüssigkeit ein wäßriges Medium ist, in dem Wasser mindestens 30 Gew.-% des Lösungsmittels ausmacht.
- 55 19. Beschichtungslösung zur Bildung einer thermographischen Bilderzeugungsschicht, die ein organisches Silbersalz, ein Reduktionsmittel für Silber-Ionen und ein Bindemittel enthält und die bei 25°C eine Viskosität von 500 mPa·s bis 500 000 mPa·s bei einem Geschwindigkeitsgefälle von 0,1 s<sup>-1</sup> und von 0,1 mPa·s bis 100 mPa·s bei einem Geschwindigkeitsgefälle von 1 000 s<sup>-1</sup> hat.

## EP 0 883 022 B1

20. Ein thermographisches Bilderzeugungselement, das durch Auftragen einer Beschichtungslösung, die ein organisches Silbersalz, ein Reduktionsmittel für Silber-Ionen und ein Bindemittel enthält und die bei 25°C eine Viskosität von 500 mPa·s bis 500 000 mPa·s bei einem Geschwindigkeitsgefälle von 0,1 s<sup>-1</sup> und von 0,1 mPa·s bis 100 mPa·s bei einem Geschwindigkeitsgefälle von 1 000 s<sup>-1</sup> hat, hergestellt wurde.

21. Photothermographisches Bilderzeugungselement, das durch Auftragen einer Beschichtungslösung, die ein organisches Silbersalz, ein Reduktionsmittel für Silber-Ionen, ein lichtempfindliches Silberhalogenid und ein Bindemittel enthält und die bei 25°C eine Viskosität von 500 mPa·s bis 500 000 mPa·s bei einem Geschwindigkeitsgefälle von 0,1 s<sup>-1</sup> und von 0,1 mPa·s bis 100 mPa·s bei einem Geschwindigkeitsgefälle von 1 000 s<sup>-1</sup> hat, hergestellt wurde.

### Revendications

1. Procédé de revêtement pour la préparation d'un élément formateur d'image thermographique ou photothermographique, comprenant l'étape consistant à:  
appliquer un liquide contenant un sel d'argent organique et un liant, et présentant une viscosité à 25°C de 500 mPa·s à 500 000 mPa·s à un taux de cisaillement de 0,1 s<sup>-1</sup> et de 0,1 mPa·s à 100 mPa·s à un taux de cisaillement de 1000 s<sup>-1</sup>.

2. Procédé selon la revendication 1 dans lequel le dit liquide contient de plus un agent réducteur pour l'ion argent.

3. Procédé selon la revendication 1 ou 2 dans lequel le dit sel d'argent organique est un sel d'argent d'un acide carboxylique organique.

4. Procédé selon l'une quelconque des revendications 1 à 3 dans lequel le dit liquide contient de plus un halogénure d'argent photosensible.

5. Procédé selon l'une quelconque des revendications 1 à 4 dans lequel le dit liquide présente une viscosité à 25°C de 500 mPa·s à 300 000 mPa·s à un taux de cisaillement de 0,1 s<sup>-1</sup>.

6. Procédé selon la revendication 5 dans lequel le dit liquide présente une viscosité à 25°C de 1000 mPa·s à 100 000 mPa·s à un taux de cisaillement de 0,1 s<sup>-1</sup>.

7. Procédé selon la revendication 6 dans lequel le dit liquide présente une viscosité à 25°C de 1000 mPa·s à 30 000 mPa·s à un taux de cisaillement de 0,1 s<sup>-1</sup>.

8. Procédé selon l'une quelconque des revendications 1 à 7 dans lequel le dit liquide présente une viscosité à 25°C de 0,2 mPa·s à 100 mPa·s à un taux de cisaillement de 1000 s<sup>-1</sup>.

9. Procédé selon la revendication 8 dans lequel le dit liquide présente une viscosité à 25°C de 1 mPa·s à 80 mPa·s à un taux de cisaillement de 1000 s<sup>-1</sup>.

10. Procédé selon l'une quelconque des revendications 1 à 9 dans lequel le dit liquide contient des fines particules solides présentant une taille de 0,001 µm à 10 µm à une concentration de 10 à 80% en poids.

11. Procédé selon la revendication 10 dans lequel le dit liquide contient des fines particules solides présentant une taille de 0,01 µm à 5 µm à une concentration de 10 à 80% en poids.

12. Procédé selon la revendication 10 ou 11 dans lequel le dit liquide contient des fines particules solides à une concentration de 15 à 50% en poids.

13. Procédé selon la revendication 12 dans lequel le dit liquide contient des fines particules solides à une concentration de 20 à 50% en poids.

14. Procédé selon l'une quelconque des revendications 1 à 13 dans lequel le dit liquide contient des fines particules solides non-sphériques à une concentration de 0,1 à 50% en poids.

15. Procédé selon la revendication 14 dans lequel le dit liquide contient des fines particules solides non-sphériques

## EP 0 883 022 B1

à une concentration de 0,5 à 20% en poids.

16. Procédé selon l'une quelconque des revendications 1 à 15 dans lequel le dit liquide contient un latex de polymère en quantité d'au moins 50% en poids du liant total.

5

17. Procédé selon la revendication 16 dans lequel le latex de polymère présente un teneur en humidité d'équilibre jusqu'à 2% en poids à 25°C et HR 60%.

18. Procédé selon l'une quelconque des revendications 1 à 17 dans lequel le liquide est un milieu aqueux dans lequel l'eau compte pour au moins 30% en poids du solvant.

10

19. Solution pour former une couche formatrice d'image thermographique, contenant un sel d'argent organique, un agent réducteur pour l'ion argent et un liant, et présentant une viscosité à 25°C de 500 mPa·s à 500000 mPa·s à un taux de cisaillement de 0,1 s<sup>-1</sup> et de 0,1 mPa·s à 100 mPa·s à un taux de cisaillement de 1000 s<sup>-1</sup>.

15

20. Élément formateur d'image thermographique qui a été préparé par application d'une solution de revêtement contenant un sel d'argent organique, un agent réducteur pour l'ion argent et un liant, et présentant une viscosité à 25°C de 500 mPa·s à 500000 mPa·s à un taux de cisaillement de 0,1 s<sup>-1</sup> et de 0,1 mPa·s à 100 mPa·s à un taux de cisaillement de 1000 s<sup>-1</sup>.

20

21. Élément formateur d'image photothermographique qui a été préparé par application d'une solution de revêtement contenant un sel d'argent organique, un agent réducteur pour l'ion argent, un halogénure d'argent photosensible et un liant, et présentant une viscosité à 25°C de 500 mPa·s à 500000 mPa·s à un taux de cisaillement de 0,1 s<sup>-1</sup> et de 0,1 mPa·s à 100 mPa·s à un taux de cisaillement de 1000 s<sup>-1</sup>.

25

30

35

40

45

50

55

FIG. 1

